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(54) A catalyst for reducing nitrogen oxides in combustion gases and a method for its production.

(57) A catalyst for reducing oxides of nitrogen in combustion gases comprising compounds of titanium and vanadium in particles of single monodispersed crystals, all having the same linear dimension between 50Å and 200Å and lacking internal porosity, the catalyst being obtained irradiating with a CO₂ laser beam metallo-organic compounds of titanium and vanadium together with a jet of a sensitizer gas at an absorption band in the spectral zone between 940 and 1,000 cm⁻¹.

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The present invention concerns a catalyst for reducing nitrogen oxides in combustion gasses and a method for its production; in particular, it concerns a catalyst for the selective reduction of nitrogen oxides with ammonia and the method for its production.

The technical field relative to the present invention is that of testing nitrogen oxide emissions in the discharge gasses of thermo-electric stations, incinerators, and nitric acid production plants, testing carried out by the process of selective catalytic reduction by ammonia. In this field good catalysts are known containing metallic oxides, especially of vanadium supported on a base of titanium dioxide.

Generally the conventional catalysts are constituted by a base of titanium oxide (Anatase) on which a single coating of vanadium oxide is deposited by impregnation. In the patent application No.21673 A/89 the same applicant claims a vanadium oxide catalyst on a base of single monodispersed titanium oxide crystals, that is all having substantially the same dimension, ultrafine and non aggregate and in addition a method for producing the said catalyst by laser is claimed; once produced, the titanium oxide crystals are impregnated with high concentrations of vanadium oxide without giving rise to V_2O_5 precipitates.

The principal drawback of all impregnated catalysts is that their low thermal stability involves the reduction of the specific surface following their prolonged use and of the segregation of V_2O_5 crystals. This segregation reduces the selectivity of the SCR reaction and contributes to the oxidation of SO_2 to SO_3 , creating, therefore, problems of corrosion in the cooler parts of the boiler or of the turbine and stoppage problems in the catalytic reaction vessel and in the heat exchanger due to the formation of $(NH_4)_2HSO_4$ and $(NH_4)_2S_2O_7$.

The invented catalyst obviates the cited drawbacks; it, as claimed, comprises crystals of titanium oxide and vanadium oxide together ($Ti_{1-x}V_xO_2$) in which the vanadium is intimately bound to the titanium in the crystalline lattice (in the following of this description the said oxide of titanium and vanadium will be called "mixed oxide"). The crystals have an anatase crystalline structure, are monodispersed, have an average diameter between 50 Å and 200 Å inclusive, according to the conditions of the process, surface area of between 240 m²/g and 90 m²/g inclusive, and do not show internal porosity.

As disclosed in said patent application, the production method comprises the laser ray pyrolysis of vapors of suitable compounds of titanium and vanadium. In the present case the method comprises the pyrolysis of a jet of mixed vapors of a metallo-organic and or inorganic compound of titanium and a metallo-organic and or inorganic compound of vanadium by means of a laser ray; the powders obtained are calcined at the appropriate temperature. The quantity of the titanium and vanadium in the powder obtained by pyrolysis may be varied by varying the temperature of one of the said compounds with respect to the temperature of the other compound (the quantity of the compound which has the higher temperature increases), or else one controls the rate of flux of the gas carrier for both the said compounds.

The percentage by weight of the vanadium with respect to the total weight is between 0.1% and 30% inclusive, preferably between 5% and 20%.

More particularly, the production method comprises the phases of: a) irradiation of a jet of metallo-organic and/or inorganic compounds of titanium and of metallo-organic and/or inorganic compounds of vanadium in appropriate proportions by a continuous emission laser beam; b1) generation of a flux of inert gas, preferably of argon, to keep the said jet of the said compounds guided in order that the said compounds absorb the laser radiation in resonance in the region of intersection between the laser ray and the said jet; b2) if the said compounds do not absorb the laser radiation in resonance, alternatively, mixing the said compounds with a gas, such as ethylene or sulphur hexafluoride, which presents an absorption band in the spectral region between 940 and 1,000 cm⁻¹, in this way the said gas absorbs the laser radiation and acts as a sensitizer for the transfer of energy to the compounds of titanium and vanadium. In the said region high temperatures (500-1,500 °C) are reached and the chemical reaction takes place which leads to the formation of particles of mixed oxides of titanium and vanadium, monocrystalline, anatase and of dimensions variable from a few tens of to a few hundred Ångstrom. The dimensions of the particles can be varied by varying the stay time, that is the time for which the said compounds remain under the action of the beam laser (the greater the stay time the greater the dimensions of the particles), the power of the laser beam and the efficiency of the sensitizer gas. The stay time (between 1 and 40 ms) is itself controllable on the basis of the magnitude of the flux of the said compounds, of the gas carrier (for example, from 100 to 1,000 sccm) and of the sensitizer gas (for example, from 200-1,000 sccm for C_2H_4 and from 10-100 for SF_6), of argon (for example, from 1,000-10,000 sccm) on the basis of the diameter of the laser beam section (5-20mm) and the reagent emission nozzle section (from 3×10^{-2} to 3 cm²). The power of the laser beam will be proportional to the flux of the said compounds; for example, for the production of a few kilograms of industrial grade catalyst, the power of the laser will be of a few kilowatts. (Note: sccm = standard cubic centimeter per minute).

The powders thus obtained are calcined at the appropriate temperature.

The ways of employing the invented catalysts are substantially the same as the ways of using described in the above mentioned patent application with the direction that the combustion gasses are sent onto the catalyst at temperatures between 150 and 450 °C, preferably between 200 and 400 °C.

The principle advantages of the invented catalyst are: the high specific surface given by the absence of impregnation and, consequently, the high catalytic activity which allows a strong removal of NO from the combustion gasses; the rapidity of the production process, because there is not the phase of impregnation necessary in other known methods.

To the goal of illustrating in detail the invention reported here there follows a few specific examples, not limiting, concerning either the production method or the performance of the catalyst.

With the premise that, to carry out the catalysis function tests, the following experimental conditions were adopted:

A gas containing either 2.7% or 0.3% in O₂, 700 ppm of NO and 700 ppm of NH₃ (ppm = parts per million expressed by volume) is fed onto a bed of a catalyst at a space velocity of 1.1x10⁵/h at a given temperature. The concentration of NO at the entrance and the exit of the reaction vessel is measured so as to estimate the magnitude of removal expressed as follows:

$$100 \times [(NO)_{in} - (NO)_{out}] / (NO)_{in}$$

Further the data set out in the above mentioned patent application which show how the catalytic activity of the powder of mixed oxide Ti_xV_{1-x}O₂ is comparable to and even superior to that of the catalysts obtained by impregnation are reported for comparison.

EXAMPLES 1 - 2 - 3 - 4 - 5 - 6

Production of a series of catalysts with varying proportions of vanadium, with characteristics reported as follows:

TABLE 1

Example	%V	S(m ² /g)	Ti(°C)
1	0.4	112	198
2	1.2	143	196
3	6.5	90	194
4	10.5	95	192
5	11.5	121	190
6	15.8	111	180
(%V is the percentage by weight of vanadium with respect to the total weight).			

A flux of ethylene (200sccm) drags into the reaction chamber titanium isopropoxy vapour from a container at controlled temperature in which the temperature of the liquid is maintained at the different values reported in table 1; simultaneously, a flux of ethylene (200 sccm) drags into the reaction chamber vanadyl isopropoxy vapour from another container at controlled temperature in which the temperature of the liquid is maintained at the constant value of 120 °C. The jet of mixed titanium isopropoxy and vanadyl isopropoxy vapours, spatially confined by a flux of argon (2,000 sccm) is perpendicularly irradiated by the beam of a continuously emitting CO₂ laser, of circular section (8mm) and incident power 550W; the pressure in the isopropoxy containers and in the reaction chamber is 250 torr. The powder is calcined in air at T = 400 °C for three hours.

Examples 7- 8- 9- 10- 11

Production of a series of catalysts of various proportions of vanadium, with characteristics reported in the following table 2:

TABLE 2

EXAMPLES	% V	S (m ² /g)	T _v (°C)
7	7.6	134	75
8	9.9	123	80
9	12.2	172	85
10	14.3	136	88
11	15.2	177	90

A flux of argon (300 sccm) drags titanium isopropoxy vapour into the reaction chamber from a container at controlled temperature in which the temperature of the liquid is maintained at a constant of 160°C; simultaneously, a flux of argon (300 sccm) drags vanadyl isopropoxy vapour into the reaction chamber from another container at controlled temperature in which the temperature of the liquid is maintained at the various values reported in Table 2. Such mixture is added before entering the reaction chamber, to a controlled flux of sulphur hexafluoride (15 sccm). The jet of such composition is treated as was indicated for the jet of mixed vapours at the end of the examples reported above. In this case, also, the powder is calcined in air at T = 400°C for three hours.

RESULTS

In Tables 3 and 4 the data for the conversion of NO at different temperatures for catalysts prepared according to examples 3-5-6, with the following experimental conditions are reported:

contact time	0.005 sec
total flow	80 l/h
concentration of NO	700 ppm
concentration of NH ₃	700 ppm
concentration of O ₂	0.3 and 2.7 %

Table 3

(O ₂ = 2.7%)						
T(°C)	250°C % NO	yield N ₂ O	300 °C % NO	yield NO ₂	350 °C % NO	yield N ₂ O
3	24.7	0	57.2	0	76.6	2
5	46.9	0	80.3	0	88.6	2
6	54.3	0	77.6	2	84.3	4

Table 4

(O ₂ = 0.3%)						
T(°C)	250°C % NO	yield N ₂ O	300 °C % NO	yield N ₂ O	350 °C % NO	yield N ₂ O
3	14.3	0	37.6	0	59.6	2
5	26.0	0	63.9	0	80.4	4
6	40.9	0	64.1	2	73.7	6

Reference Examples

By way of reference we use the examples set out in the above mentioned patent application which shows how catalysts based on mixed oxide Ti_xV_{1-x}O₂ have a catalytic efficiency comparable or superior to

those catalysts obtained by the impregnation of ultra fine powder TiO_2 above all for percentages of vanadium greater than or equal to 11% and temperature greater than 300°C .

T ($^\circ\text{C}$)	% by weight of V_2O_5	with % of NO
250	10	50
300	10	83
350	10	66

Claims

1. A catalyst for reducing nitrogen oxides in combustion gasses comprising compounds of titanium and vanadium characterised in that the said compounds are particles of titanium and vanadium oxides in the form of single monodispersed crystals, all substantially having the same ultra fine linear dimension between 50\AA and 200\AA and lacking internal porosity.
2. A catalyst according to Claims 1 characterised in that the said particles of titanium and vanadium oxides have a surface area of almost $90\text{m}^2/\text{g}$.
3. A catalyst according to Claims 1 and 2 above characterised in that the vanadium is contained in the form of anatase titanium and vanadium oxide crystals as a percentage by weight between 1% and 30%.
4. A method for producing the catalyst defined in the claims above in which titanium and vanadium oxide powders are obtained by irradiating a jet comprising metallo-organic and or inorganic compounds of titanium and metallo-organic and or inorganic compounds of vanadium with a continuous emission CO_2 laser beam characterised in that the said beam laser irradiates simultaneously the said jet and a sensitizer gas with an absorption band in the spectral zone between 940 and $1,000\text{ cm}^{-1}$.
5. A method according to Claim 4 characterised in that the period of time for which the said compounds are under the action of the laser beam is controlled varying one or more together: the flux of said titanium and vanadium compounds; the flux of the said gas sensitizer; the flux of the said inert gas; the section of the laser beam.
6. A method according to Claims 4 and 5 characterised in that the dimensions of the said particles can be varied varying the efficiency of the said gas sensitizer.
7. A method according to claims from 4 to 6 characterised in that the relationship between titanium and vanadium in the titanium and vanadium oxide is varied varying the temperature of one of the said compounds with respect to the other.
8. A method according to the preceding claims characterised in that the said particles can be mixed oxides containing metals other than vanadium, such as tungsten, iron, niobium, molybdenum.



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EUROPEAN SEARCH REPORT

Application Number

EP 92 10 9335

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D, Y	EP-A-0 417 538 (ENTE NAZIONALE PER L'ENERGIA ELETTRICA)	1, 8	801D53/36
A	* the whole document *	2-5	801J23/00
	---		801J23/22
Y	EP-A-0 211 443 (SIEMENS AG)	1, 8	801J37/34
	* column 2, line 36 - line 45; claims 1-3 *		

A	EP-A-0 403 879 (SIEMENS AG)	1, 3, 8	
	* claims 1, 2 *		

A	EP-A-0 314 392 (BABCOCK-HITACHI K.K.)	1, 3, 8	
	* claim 1 *		

			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			801D
			801J
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	08 SEPTEMBER 1992	CUBAS ALCARAZ J. L.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention	
X : particularly relevant if taken alone		E : earlier patent document, but published on, or	
Y : particularly relevant if combined with another		after the filing date	
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P : intermediate document		* : member of the same patent family, corresponding document	

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